The Asymmetric Rotor. IX. The Heavy Water Bands at 2787 cm^{-1} and 5373 cm^{-1}*

K. KEITH INNES AND PAUL C. CROSS
Department of Chemistry and Chemical Engineering, University of Washington, Seattle, Washington

AND

PAUL A. GIGUÈRE†
California Institute of Technology, Pasadena, California

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The combination band (110) of the two stretching fundamentals of D_2O is reported and analyzed to yield $\nu_0=5373.2$ cm^{-1} and the excited state moments of inertia 1.910, 3.931, and 5.929×10^{-40} g cm^2. The same method of analysis applied to the unsymmetrical fundamental band (100) envelope gives $\nu_0=2787.5$ cm^{-1} and the excited state moments 1.881, 3.876, and 5.843×10^{-40} g cm^2.

INTRODUCTION

A SUMMARY of the work to date on the analysis of vibration and rotation spectra of heavy water vapor is presented in Table I.

Fuson, Randall, and Dennison[1] obtained an expression for the effective reciprocal moments of inertia of heavy water as functions of the vibrational quantum numbers by computing the isotope effect on the constants in the analogous expression for water. Using the inertial constants for the ground state as given by this expression and applying a crude classical correction for centrifugal distortion they obtained calculated "key" energies as an aid to the building of an "experimental" term scheme from the pure rotation spectrum. The difference between the calculated and constructed term values are given in the column $W-W_k$ of their Table IV. They did not, apparently, investigate the possibility of minimizing these differences with the objective of obtaining "best values" of the inertial constants. For instance, an inspection of these differences for the low τ-levels indicates that they could be consistently reduced by an increase of 0.01 cm^{-1} in the inertial constant C. In fact, such an increase was found necessary by King[2] in his band envelope analysis of the bending fundamental by punched-card machine methods.

DN[3] obtained two infrared active fundamentals at high resolution and analyzed both by deducing the excited state term values in the manner of Fuson, Randall, and Dennison, apparently using the experimental term values for the ground state given in reference 1. They then chose effective moments which best represented their excited state term schemes at low J values, remarking that the moments given by King yielded a poorer fit for the (001) band.

This paper presents the results of the first analysis of a combination band of heavy water as well as an investigation of the data for the unsymmetrical stretching fundamental[3] by the band envelope method.[4]

EXPERIMENTAL

Frequencies of the absorption peaks observed in the region 5250 to 5490 cm^{-1} are recorded in Table II.

TABLE I. Vibration-rotation parameters of heavy water.

Analysis data	a a	b c	b c	d d	d d	e d	e e
$(n_3n_1n_2)$	(000)	(000)	(001)	(001)	(100)	(100)	(110)
ν_0 obs			1179	1178.3	2787.2	2787.5	5373.2
ν_0 calc			1178.8	1178.8	2787.6	2787.6	5372.8
A_{obs}	15.38	15.38	16.50	16.60	14.88	14.88	14.65
B_{obs}	7.25	7.25	7.33	7.35	7.24	7.22	7.12
C_{obs}	4.83	4.84	4.79	4.84	4.84	4.79	4.72
A_{calc}	15.385	15.385	16.50	16.50	14.88	14.88	14.59
B_{calc}	7.255	7.255	7.33	7.33	7.21	7.21	7.12
C_{calc}	4.830	4.830	4.77	4.77	4.77	4.77	4.71
Δ_{obs}	0.115	0.105	0.329	0.288	0.035	0.086	0.088
Δ_{calc}	0.105	0.105	0.329	0.329	0.088	0.088	0.088

[a] See reference 1.
[b] See reference 2.
[c] E. F. Barker and W. W. Sleator, J. Chem. Phys. 3, 660 (1935).
[d] See reference 3.
[e] This work.

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† Now at the Department of Chemistry, Laval University, Quebec, Canada.
[1] Fuson, Randall, and Dennison, Phys. Rev. **56**, 982 (1939).
[2] G. W. King, J. Chem. Phys. **15**, 85 (1947).
[3] F. P. Dickey and H. H. Nielsen, Phys. Rev. **73**, 1164 (1948). Hereafter referred to as DN.
[4] Allen, Cross, and Wilson, J. Chem. Phys. **18**, 691 (1950).

The heavy water used was 99.5 percent pure; the absorption cell was one meter long and the pressure, about 200 mm. The spectrum was studied with an automatic recording vacuum spectrometer[5] using the first order of an échelette grating with 7500 lines to the inch. Overlapping orders were eliminated successfully by means of a special plastic filter[6] kindly supplied by the Polaroid Corporation. The photosensitive element was a lead sulfide cell operating at room temperature. The resolution was of the order of 2 cm^{-1} with a slit width of 0.05 cm corresponding to 0.9 cm^{-1} in the region covered. Calibration for wavelength was based on the infrared lines of argon. Scanning was done at the rate of 15A per minute.

The present band coincides almost exactly with the fairly intense $\nu_2+\nu_3$ band of ordinary water, which may explain why it has not been reported before. For the same reason it was important to avoid all absorption due to atmospheric moisture.

ANALYSIS

Absorption in the region 5250 to 5500 cm^{-1} was evidently due to an A-type band which was accordingly given the combination assignment (110). The band center calculable from potential constants[7] for the molecule was 5372.8 cm^{-1}.

The Fuson, Randall, and Dennison expression yielded a first approximation to the moments of the upper state as listed in the last column of Table I. Using these, the observed ground state constants of King and published tables,[8] the energies of permitted transitions were calculated. The trial spectrum was completed with the calculation of relative line intensities.[9] To be consistent with the analysis of King, a centrifugal distortion correction was not employed.

Preparation of a table of derivatives of upper state energies with respect to the inertial constants facilitated adjustment of the computed spectrum to a best fit of the data. That best fit is presented under the data in Fig. 1 in which all transitions (about 150) arising from levels up through $J=12$ and having intensity greater than 0.5 (on an arbitrary scale) are included. The excited state constants giving rise to that spectrum are also listed in the last column of Table I.

King assumed that rigid rotor energies could be used

TABLE II. Observed absorption peaks of the combination band $\nu_1+\nu_3$ of heavy water (ν_{vac}, cm^{-1}).*

5253.6	5374.9
5259.4	5376.1
5261.1	5380.2
5263.1	5383.1
5265.1	5385.2
5271.2	5389.7
5274.0	5393.5
5276.6	5396.2
5278.0	5398.8
5280.2	5403.9
5282.7	5406.3
5284.7	5407.9
5288.7	5411.0
5290.9	5413.3
5294.3	5415.3
5296.9	5416.8
5299.3	5422.6
5301.3	5426.6
5303.5	5430.9
5305.9	5433.5
5309.3	5437.2
5313.9	5438.0
5317.2	5440.9
5319.2	5444.2
5321.7	5445.6
5327.2	5449.0
5328.4	5453.2
5332.4	5456.2
5333.8	5458.8
5338.0	5460.2
5339.6	5461.9
5344.4	5466.8
5346.2	5468.5
5348.9	5471.9
5351.4	5474.3
5354.5	5477.7
5357.5	5480.5
5361.0	5481.9
5363.7	5485.8
5365.9	5487.3
5369.7	5491.8
5371.3	5495.5

* Computed results are not included here. Positions and intensities of rotational transitions may be calculated by using the constants of the last column of Table I with tables in references 8 and 9.

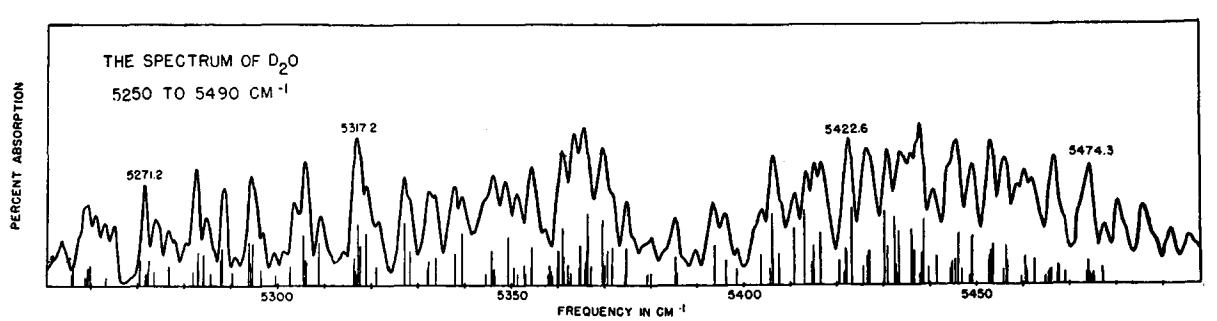

FIG. 1. Calculated and observed combination band $\nu_1+\nu_3$ at 5373.2 cm^{-1}.

[5] Badger, Zumwalt, and Giguère, Rev. Sci. Instr. **19**, 861 (1948).
[6] Blout, Amon, Shepherd, Thomas, West, and Land, J. Opt. Soc. Am. **36**, 460 (1946).
[7] B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).
[8] King, Hainer, and Cross, J. Chem. Phys. **11**, 27 (1943).
[9] Cross, Hainer, and King, J. Chem. Phys. **12**, 210 (1944).

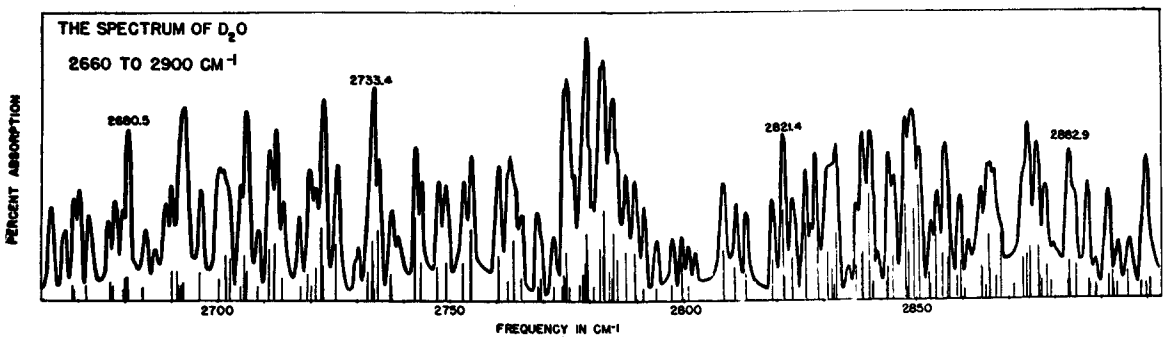

FIG. 2. Calculated and observed perpendicular stretching fundamental at 2787.5 cm^{-1}. (Experimental curve according to Dickey and Nielsen (see reference 3)).

in such analyses without serious error because important lines arise from levels of low τ-value for which distortion is small and, in any case, discrepancies tend to cancel in the term differences.

The effect on *this* spectrum of the classical centrifugal correction of Cross[10] was observed by correcting each energy level of both states and recalculating the spectrum. Only one-fourth of the lines were shifted by as much as one-fifth of a wave number and only a fourth of those by more than two-fifths of a wave number. It should be pointed out that King analyzed a parallel-type band for which allowed transitions are between levels of more widely separated τ-values than for the band considered above. This circumstance will decrease the effect of canceling of the corrections which, themselves, amount to as much as eight wave numbers for some levels important in the spectrum.

The puzzling lack of agreement of the two methods used for the analysis of the 1179 cm^{-1} band led to a preliminary survey of the data given by DN. Energies for ground and excited states were calculated using, in turn, constants given by DN and King. Resulting transitions were compared with experimental positions of the lines as identified by DN. Though the analysis was not pursued it appeared that the constants given by King led to a better fit of the data and that, especially for $J=4$, 5, 6, a number of peaks had been associated with the wrong transitions in the later analysis.[3] This conclusion is supported by the fact that one would not expect $I_C(=h/8\pi^2cC)$ to be smaller for the excited than for the ground state. Indeed, one may observe that for all water bands analyzed the reverse is the case.[7] The magnitude of the disagreement of calculated and observed Δ's also seems unreasonably large. This shows up in the discrepancies between observed and predicted values of the inertial constants.

For these reasons it was thought worthwhile to reinvestigate the DN data for ν_3, extending the analysis, as for the (110) band, through $J=12$ for all lines of appreciable intensity. The fit illustrated in Fig. 2 was obtained with the constants listed in column seven of Table I. Note that the constants employed for this best fit preserve agreement between the calculated and observed values of Δ.

The assignment of transitions to observed peaks by DN checked well with ours within 60 cm^{-1} of either side of the band center. However, for transitions involving $J=5$ or greater, the agreement is sometimes poor. For example, the transition $5_{-3}-6_{-4}$ contributed to a peak at 2710.9 in our analysis but was assigned to 2705.9 cm^{-1} by DN.

The band envelope method depends only on the adjustment of seven parameters: the band center and the three inertial constants of each of the two states. Difficulties of building term schemes from such spectra are illustrated in the two figures from which it is seen that, in general, each peak is an envelope of several lines.

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[10] P. C. Cross, Phys. Rev. 47, 7 (1935).